

PROGRESS REPORT FORM

Via e-mail if possible:

1. PI's Name and Affiliation: **Prasad Varanasi, State University of New York at Stony Brook.**
2. Title of Research Grant: **Laboratory Spectroscopy Related to the ARM Program**
3. Scientific Goal(s) of Research Grant (Maximum of 200-300 words): **To provide accurate spectroscopic data on water vapor and other important greenhouse gases to the ARM Science Team. The data obtained with high precision in the laboratory (a) enable us to validate the existing spectroscopic database, and more importantly (b) aid the Science Team, in particular, and the atmospheric modeler, in general, in developing accurate models for the clear-sky atmosphere and in properly analyzing the atmospheric measurements made at various CART sites.**
4. Accomplishments: **Measurements of the spectral line parameters of water vapor in the 950-2067 and 3000-4050 cm^{-1} spectral regions; Validation of the *HITRAN* database on the short-wave absorption bands of water vapor; Successful deployment of the laser-photo-acoustic study of the short-wave spectrum of water vapor in saturated and super-saturated levels.**
5. Progress and accomplishments during last twelve months

Water Vapor Line Intensity Corrections and Rovibrational Assignment Updates of the Shortwave HITRAN and GEISA Databases.

Systematic differences were found between the absolute intensities of most of the water vapor lines in the $8036\text{--}22657\text{ cm}^{-1}$ region listed in the HITRAN-96 database and those reported in the five original articles which were the sources for the HITRAN and GEISA databases. The 5 articles reporting measured line intensities all used “measurement” units of $\text{cm}^{-1}/(\text{cm-atm})$ at room temperature. Three different conversion errors were made when the measured intensities were transformed into $\text{cm}/\text{molecule}$ at 296 K, the units used by the databases. We have developed corrections to the HITRAN and GEISA line intensities to bring them into compliance with the measured intensities. These corrections only apply to assigned lines of the main isotopomer of water reported in these 5 articles, which is over 97% of the absorption intensity in the databases in each of the 5 cm^{-1} intervals of these articles. The correction

increases the database intensities by a constant 14.4% in the 9500-11500 cm^{-1} region, and by a constant 8.7% in the 11500-13000 cm^{-1} region. In the 8036-9500, 13000-16500, and 16500-25250 cm^{-1} regions, the intensity corrections are not constant, but depend on the lower state energy level, E'' , of each line. The correction we found in these regions is $\exp[-E''(2hc/k(1/T - 1/T'))]$, where $T=296\text{K}$ and T' is the measurement temperature. This correction becomes significant at higher values of E'' ; it decreases line intensities in HITRAN and GEISA by about 19% at $E''=1400\text{ cm}^{-1}$. A corrected line list has been posted on HITRAN's internet site (<http://www.hitran.com>). These corrections do not apply to the many unassigned water lines on the databases in this spectral region. Schwenke (*J. Mol. Spec.* **190**, 397-402, 1998) has given rovibrational assignments to many of these unassigned lines in this entire spectral region. Using the *ab initio* computed line list on his internet site (<http://ccf.arc.nasa.gov/~dschwenke>), we have included assignments on the corrected line list for all 71 unassigned lines in the region of the important 0.94 micron water band. Polyansky *et al.* (*J. Mol. Spec.* **189**, 291-300, 1998) have also assigned over 600 of the unassigned lines in the 13200-16500 cm^{-1} region. There are many disagreements on assignments between these two publications; however, a detailed comparison of them and Schwenke's *ab initio* line list shows a large number of agreements, at least for the lower state assignment and energy level, E'' , which is of primary importance for atmospheric applications. A line list of "consensus" assignments in the 13200-16500 cm^{-1} region is in preparation for consideration of inclusion on the HITRAN and GEISA databases.

Measurement of the Absorption Characteristics of Water Vapor Near Saturation.

A number of experiments were carried out to establish the performance of the water vapor absorption cell and the photo-acoustic laser-spectroscopic procedure for measuring the absorption of water vapor. After measuring the temperature profiles in the cell filled with dry air the cell was filled with air and saturated with water. Photo-acoustic absorption measurements at several wavelengths in the 815 to 820 nm region were performed with saturated water vapor at a number of temperatures from 15 to 35 C in steps of 5C. For these tests the laser wavelength was scanned across the individual absorption lines in 1 pm (500 MHz, or $.017\text{ cm}^{-1}$) steps. These results show very good performance of the photo-acoustic absorption system. Experiments with supersaturated water are being setup now.

Measurements of the Infrared Spectral Lines of Water Vapor at Atmospheric Temperatures.

We obtained new experimental data on the intensities, self- and air-broadened half-widths, pressure-induced shifts of the spectral lines of water vapor located between 1260 and 2065 cm^{-1} . The spectra were taken at 252, 273, and 296 K. We have determined the dependence of these important spectral line

parameters upon temperatures. At 296 K we report measurements on 342 lines with $0 \leq J \leq 12$. The air-broadened line widths range from 0.0122 to 0.1062 cm^{-1} , and the shifts are between -0.0538 to 0.0413 cm^{-1} . Of these lines we were able to determine temperature dependence of the line broadening parameters for 183 lines. The air-broadened line width data are compared with the entries in the HITRAN database. The line shift data we have measured show a distinct J-dependence. We also report many self-broadened line width data that are either missing or apparently erroneous in the existing spectroscopic databases.

We also measured line positions, line strengths, self-broadened line widths and self-induced lineshifts of 268 lines in the 3600-4050 cm^{-1} region. The line strengths and linewidths are compared with the HITRAN data and those reported by other investigators. The self-broadened linewidths in the ν_1 band (at 2.7 μm) seem to be smaller by more than 5% than those in the ν_2 band (at 6.3 μm) for lines with the same rotational quantum numbers, thereby suggesting a small dependence upon the vibrational quantum number of the upper state in the two fundamental bands. Our line shift data are apparently the first ever measured of these lines. The temperature dependence of line parameters has also been a first of its kind of measurement.

Absorption Cross-sections of C_2F_6 and HFC-134a at Atmospheric Conditions

Spectral absorption cross-sections, k_v ($\text{cm}^{-1} \text{ atm}^{-1}$), have been measured in the 8.0 and 8.96 μm bands of C_2F_6 , and in the 8.0 and 9.23 μm bands of HFC-134a, using a high-resolution Fourier-transform spectrometer. Temperature and total (N_2 -broadening) pressure have been varied to meet the conditions representative of the terrestrial atmosphere and often encountered in atmospheric remote sensing experiments such as satellite-based solar-occultation measurements.

Infrared Line Parameters of Greenhouse Gases at Atmospheric Temperatures

We have performed several new measurements of intensities and air-broadened linewidths of spectral lines in the important fundamental bands of CO, CO_2 , N_2O , CH_4 , NH_3 , and C_2H_2 at atmospheric temperatures between 200 and 296 K. The temperature dependence of the line parameters is presented. The new data are compared with the entries in the HITRAN and GEISA databases.

6. As appropriate attach one or so electronic figures with paragraph discussions highlighting current research. Label with PI name, affiliation, and year. We will use these in presentation materials.

7. List all *refereed* publications either submitted or published during the *current* grant FY that acknowledge DOE ARM support. Two copies of all submitted papers should accompany the progress report. (Two reprints of all published papers should be submitted to the ARM Science Director when reprints are received. If this wasn't done at the time please include reprints with the progress report.*)

N. Jacquinet-Husson et al. (with Nemtchinov and Varanasi among the many coauthors), "The 1997 spectroscopic GEISA databank," *JQSRT* **62**, 205 (1999).

L. P. Giver, C. Chackerian, Jr., and P. Varanasi, "Visible and near-infrared H_2^{16}O line intensity corrections for HITRAN-96," *Journal of Quantitative Spectroscopy and Radiative Transfer*, **66**, 101-105 (2000).

8. List all published (either paper or web-based) extended abstracts in the current FY that acknowledge DOE ARM support. Two copies of each should accompany the progress report*.

V. Nemtchinov and P. Varanasi, "Absorption Cross-section Data Needed for Remote Sensing CF_4 in the Atmosphere," (in preparation).

V. Nemtchinov and P. Varanasi, "Spectral Absorption Coefficients in the 12.6 μm Band of CCl_4 at Atmospheric Temperatures," (in preparation).

V. Nemtchinov and P. Varanasi, "Spectral Absorption Cross-sections in the Thermal Infrared Bands of the 12.6 μm Band of HFC-134a at Atmospheric Temperatures," (in preparation).

Q. Zou, C. Sun, and P. Varanasi, "Thermal infrared spectra of CO_2 and H_2O at atmospheric temperatures," Paper DO3, Atmospheric Spectroscopy Applications Conference, Reims, France, 1-3 September 1999.

V. Nemtchinov, Q. Zou, C. Sun, and P. Varanasi, "Thermal infrared cross-sections of C_2F_6 at atmospheric temperatures," Paper DP19, Atmospheric Spectroscopy Applications Conference, Reims, France, 1-3 September 1999.

C. Sun, Q. Zou, and P. Varanasi, "Intensity and linewidth measurements in the 13.7 μm bands of C_2H_2 at planetary atmospheric temperatures," Atmospheric Spectroscopy Applications Conference, Reims, France, 1-3 September 1999.

L. P. Giver, C. Chackerian, Jr., and P. Varanasi, "Water vapor line intensity corrections for HITRAN-96: 0.40 to 1.24 μm (8036 to 25250 cm^{-1})," Paper DP4, Atmospheric Spectroscopy Applications Conference, Reims, France, 1-3 September 1999. Varanasi was the invited speaker of this presentation.

P. Varanasi, "A validation of the current spectroscopic databases for satellite remote sensing," Talk given at the ADEOS/ILAS Symposium/workshop, Kyoto, December 6-10, 1999.

L. P. Giver, C. Chackerian, Jr., D. W. Schwenke, and P. Varanasi, "Some new concerns regarding the shortwave spectroscopic database for water vapor and its implications on atmospheric climate modeling," Oral presentation at the AGU Fall Meeting in San Francisco, CA, December 13-17, 1999.

Q. Zou, P. Varanasi, and C. Sun, "Experimental study of self- and air-broadened lines of water vapor," Paper presented at the Sixth Biennial HITRAN Database Conference, Cambridge, MA, June 19-21, 2000.

P. Varanasi, "Some new laboratory measurements and their effect upon the spectroscopic database," Paper P19 presented at the Sixth Biennial HITRAN Database Conference, Cambridge, MA, June 19-21, 2000.

C. Sun, Q. Zou, and P. Varanasi, "Intensity and linewidths Measurements in the 13.7 μm bands of C_2H_2 at planetary temperatures," Paper P28 presented at the sixth biennial HITRAN database conference, Cambridge, MA, June 19-21, 2000.

L. P. Giver, C. Chackerian, Jr., D. W. Schwenke, and P. Varanasi, "Water vapor line intensity corrections and rovibrational assignment updates of the shortwave HITRAN and GEISA databases," Oral presentation (by Varanasi) in Session E of the International Radiation Symposium, St. Petersburg, Russia, 24-29 July 2000.

P. Varanasi, "Summary of water vapor spectroscopy," Invited paper in Session E of the International Radiation Symposium, St. Petersburg, Russia, 24-29 July 2000.

P. Varanasi, B. Ranganayakamma, S. Mathur, and C. R. Prasad, "Measurement of the absorption characteristics of water vapor near saturation," Paper to be presented in Session E of the International Radiation Symposium, St. Petersburg, Russia, 24-29 July 2000.

P. Varanasi, Q. Zou, and C. Sun, "Measurements of the infrared spectral lines of water vapor at atmospheric temperatures," Paper to be presented in Session E of the International Radiation Symposium, St. Petersburg, Russia, 24-29 July 2000.

P. Varanasi, Q. Zou, C. Sun, and V. Nemtchinov, "Absorption cross-sections of C_2F_6 and HFC-134a at atmospheric conditions," Paper to be presented in Session E of the International Radiation Symposium, St. Petersburg, Russia, 24-29 July 2000.

P. Varanasi, Q. Zou, C. Sun, Z. Li, and V. Nemtchinov, "Infrared line parameters of greenhouse gases at atmospheric temperatures," Paper to be presented in Session E of the International Radiation Symposium, St. Petersburg, Russia, 24-29 July 2000.

9. Please update us on the status of submitted referred publications from the previous FY progress report. (If none, note "NONE"). None.

*Via ordinary mail